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Volumetric Estimation of Phosphoric Acid

A FURTHER COMMUNICATION ON THE ESTIMATION OF PHOSPHORIC ACID
BY TITRATION OF THE AMMONIUM PHOSPHO-MOLYBDATE PRECIPITATE
WITH STANDARD ALKALI.

ISSUED BY THE
NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION
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Volumetric Estimation of Phosphoric Acid.

A Further Communication on the Estimation of Phosphoric Acid by Titration of the Ammonium Phospho-molybdate Precipitate with Standard Alkali.

BY B. W. KILGORE.

During the past four years the writer has done a large amount of work on this method,¹ and the results obtained in this laboratory for the past two years, at least by five analysts, warrant us in considering it thoroughly accurate and reliable. More recently the method has been extensively and successfully employed in experiment station and other laboratories. Some chemists, however, have not been able to secure uniformly good results with it. These appear to be mostly those who have worked the method but little, while the difficulty with others seems to be due to a misunderstanding as to how the method should be carried out.

At the last meeting of the Association of Official Agricultural Chemists, two main objections were brought against its adoption as an official method at that time. One was that it had not been tried upon a sufficient variety of fertilizers and fertilizer materials used in the trade to show that it would give as good results with all others as it had upon the materials already employed. The other objection was the one brought forward in the paper² of Mr. T. S. Gladding. Mr. Gladding had made 22 comparative tests of the volumetric method with the official gravimetric and his gravimetric methods on a microcosmic salt and various fertilizers, with closely agreeing results in all cases. He then turned over a set of precipitates to an assistant to filter and wash free from acid according to the method. It was found that the precipitates could not be freed from acid, and upon closer examination it was observed that the water was dissolving the precipitate.

The experiments, the results of which follow in the table herewith, were planned to throw light upon and if possible to settle these two questions.

With reference to the variety of materials, an examination of the publications referred to under reference (1) below will show that the method has already been worked upon quite a variety of fertilizer materials and mixed goods, which, with the

¹See proceedings of Association of Off. Agricultural Chemists, Bulletins 43, pp. 68-104; and 47, pp. 62-83, U. S. Dept. Agriculture; Bul. 119 of this Station; and Jour. Am. Chem. Soc., Vol. 16, No. 11, and Vol. 17, No. 12.

²Bulletin 49, Chem. Div. U. S. Dept. Agr., p. 75.

materials investigated in this paper, appears to include nearly all, if not all, the sources of phosphoric acid in the fertilizer trade. Besides these, the large number of results presented to the Association last year by Mr. John P. Street, and published in the Annual Report of the New Jersey Station,³ shows that the method gives good results on mixed goods. Mr. Street says: "The materials analyzed included 276 complete fertilizers, of varying composition and origin, and are believed to fairly represent the average goods on the market at the present time. The results secured were extremely satisfactory, the average results by the volumetric method being 10.72 per cent. against 10.70 per cent. by the official method. Of these results, 150 were higher by the volumetric, 113 lower, and 13 identical with the official method; the greatest variation was 0.16 per cent., and 114 samples varied less than 0.05 per cent."

The results obtained by both the gravimetric and volumetric methods on the samples reported in this paper show good agreement, except those on samples 6 and 7, (American and European manufactured Thomas slags). The American slag contained a very large amount of iron and the European one quite a considerable quantity, though not so large. When the yellow precipitates from these samples were dissolved on the filter with dilute ammonia water considerable iron remained on the filter. The results marked "a" in the table were secured by carrying these through according to the usual custom without reprecipitating to get rid of iron. These "a" results are about 0.40 per cent. higher than the corresponding volumetric ones on the American slag, and considerably higher on the European one. The "white" precipitates giving these high results were seen by color and shown by chemical test to contain iron. A second set of determinations on these samples was then made, using the same solutions from which the above results were obtained and precipitating twice with molybdic solution to get rid of iron, when results *c c* and *b* were secured. These results show close agreement with the volumetric ones. Result "*b*" still contained a small amount of iron.

It appears, then, that the volumetric method has not only given as good results on all the samples here worked, including the *very high* percentages as the gravimetric method, but on the samples containing large amounts of iron the results have been better. I might state in this connection that we have found the volumetric method to give very satisfactory results in the determination of phosphoric acid in soils, where a large amount of iron is present.⁴

Now, as to Mr. Gladding's point of telling when the precipitate has been washed sufficiently. It might be stated here also that others have had difficulty at this point, and the statement in the method as published in Bulletin 46, Chemical Division U. S. Department of Agriculture, page 14, to wash the precipitate "till no longer acid," is responsible to some extent at least for this trouble.

³Seventeenth Annual Report, p. 118.

⁴Bulletin 47, Chem. Div. U. S. Dept. Agr., p. 82.

It is well known that ammonium phosphomolybdate is slightly soluble in water, and is an acid salt, and it would therefore be impossible to get a filtrate from washing with water that would be strictly neutral to very delicate indicators like phenolphthalein. It will be found, however, that when the filtrate is allowed to drop from the neck of the funnel upon delicate litmus paper that the wash water will be neutral to litmus after 100 to 200 c. c. water has passed through. The work here reported, and that previously done by us,⁵ together with the work of Street,⁶ McDonnell, and others, shows that 150 to 250 c. c. water, and often less, has been sufficient in all cases to free the precipitates from acid. But as stated by the writer in a previous paper on washing the yellow precipitate, "There is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove the nitric acid. It is in this after-washing, when all the salts have been removed from the precipitate and as much as 600 to 700 c. c. of water has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 c. c. of water."⁷ Perhaps this will explain the difficulty which occurred in Mr. Gladding's laboratory, in that more water was used for washing than was necessary. When these large quantities of water are used, the precipitate not only passes through the filter and settles out in the filtrate, but it dissolves far more readily than when smaller amounts of water are used for washing.

In the light of the experience of the past three years, however, it does not now seem to be necessary to wash with more than 150 to 200 c. c. of water, and the smaller of these is not much more, if any, than is used in washing the yellow salt in the gravimetric method.

In the results which follow in the table, I have made an additional test of the washing question by using 200 c. c. and 500 c. c. of water and the wash solutions, and making the determinations side by side and from the same solutions. The gravimetric results used for comparison were obtained on the same solutions as the volumetric ones. The results show that 200 c. c. of water, even with these *very high percentages*, was sufficient in all cases, and that 500 c. c. of water only lowered the results slightly, when at all. When 200 c. c. of 3 per cent. ammonium and potassium nitrate solutions were used for washing, the results were practically the same as those obtained when the two quantities of water were used; but when they were washed with 500 c. c., the results, greatly to my surprise, were much lower. The results were so surprising that quite a number of them were repeated, and while they were not uniform in all cases, they were always low. We had hoped to be

⁵ Bul. 47, Chem. Div. U. S. Dept. Agr., p. 62.

⁶ Seventeenth Ann. Rep. N. J. Station, p. 118.

⁷ Jour. Am. Chem. Soc., Vol. 17, p. 958.

able to wash with a very large volume of ammonium nitrate without appreciably dissolving the precipitate or causing it to run through the filter. The filtrates from these 500 c. c. ammonium and potassium nitrate washes were perfectly clear, but on evaporation the ammonium phosphomolybdate was found to be in solution.

In these determinations three-inch Hirsch funnels, with discs of filter paper covering the bottoms, and strong suction were used in filtering. The filtrates were not tested, but other determinations on the same samples, by using ordinary funnel and filter paper without pressure, showed them to be free from acid after washing with 150 to 200 c. c. of water. These results agreed well with those obtained with the pump. All the precipitates were washed twice by decantation with dilute nitric acid and once with potassium or ammonium nitrate solution before washing with water.

In view of the results with potassium and ammonium nitrate solutions, it suggested the plan of one washing by decantation with water to take the place of washing with potassium nitrate, following the washings with dilute nitric acid.

Comparative Phosphoric Acid Results on Various Fertilizer Materials by Gravimetric and Volumetric Methods.

MATERIALS.	Gravimetric Method.	Volumetric Method.	Washed with Water.	Washed with 3 per cent Potassium Nitrate.	Washed with 3 per cent Ammonium Nitrate.	Amount of Solution Corresponding to Grams Substance used in Volumetric Method.
	<i>Per cent</i>	<i>Per cent</i>	<i>c. c.</i>	<i>c. c.</i>	<i>c. c.</i>	<i>Grams.</i>
1. Cotton-seed Meal.....	2.97					
	2.96	2.97	200			.2
		2.93	500			.2
		2.91	500			.2
2. Tankage.....	11.63					
	11.67	11.68	200			.2
		11.58	500			.2
		11.60			200	.2
		11.45			500	.2
3. North Carolina Phosphate...	18.27	18.20	200			.2
	18.27	18.20	500			.2
		18.18			200	.2
		17.88			500	.2
4. South Carolina Phosphate...	27.98	28.06	200			.2
	27.98	28.09	500			.2
		28.04			200	.2
		27.74			500	.2
5. Pennsylvania Phosphate.....	18.59	18.59	200			.2
	18.58	18.56	500			.2
		18.56			200	.2
		18.34			500	.2

Comparative Phosphoric Acid Results on Various Fertilizer Materials by Gravimetric and Volumetric Methods.—Concluded.

MATERIALS.	Gravimetric Method.	Volumetric Method.	Washed with Water.	Washed with 3 per cent Potassium Nitrate.	Washed with 3 per cent Ammonium Nitrate.	Amount of Solution Corresponding to Grams Substance used in Volumetric Method.
	<i>Per cent</i>	<i>Per cent</i>	<i>c. c.</i>	<i>c. c.</i>	<i>c. c.</i>	<i>Grams.</i>
6. Thomas Slag (American)-----	<i>a</i> { 16.38 16.43	16.05 16.00	200 500	-----	-----	.2 .2
	<i>b</i> 16.14	15.98	-----	-----	200	.2
	<i>c</i> 16.04	15.75	-----	-----	500	.2
7. Thomas Slag (European)-----	<i>a</i> { 18.15 18.08	17.98 17.97	200 500	-----	-----	.2 .2
	<i>c</i> 17.90	17.88	-----	-----	200	.2
		17.73	-----	-----	500	.2
8. Bone Meal-----	22.14	22.10	200	-----	-----	.2
	22.02	22.08	500	-----	-----	.2
		22.00	-----	-----	200	.2
		21.95	-----	-----	500	.2
9. Acid Phosphate-----	17.44	17.56	200	-----	-----	.2
		17.51	500	-----	-----	.2
		17.51	-----	-----	200	.2
		17.30	-----	-----	500	.2
10. Mixed Fertilizer-----	10.23	10.40	200	-----	-----	.2
	10.25	10.35	500	-----	-----	.2
11. Tennessee Phosphate (Low grade)-----	23.08	23.11	200	-----	-----	.2
		23.11	500	-----	-----	.2
			-----	-----	-----	.1
12. Tennessee Phosphate (High grade)-----	35.07	35.00	200	-----	-----	.1
	34.85	35.10	500	-----	-----	-----
13. Aluminum Phosphate-----	46.91	47.10	200	-----	-----	.1
	46.82	47.20	500	-----	-----	.1
	47.00	-----	-----	-----	-----	-----
14. Florida Phosphate-----	37.74	37.80	200	-----	-----	.1
	37.62	37.78	500	-----	-----	.1
15. Sodium Phosphate-----	19.97	19.96	200	-----	-----	.2
	20.07	19.90	500	-----	-----	.2
	20.03	19.76	-----	200	-----	.2
	19.97	18.69	-----	500	-----	.2
	19.82	19.90	-----	-----	200	.2
		19.80	-----	-----	500	.2

Sample No. 6, American Thomas Slag, contained a very large amount of iron. No. 7, European Slag, contained less iron.

(*a.*) Were precipitated only once with molybdic solution, and the "white" precipitates were contaminated with iron. (*b. c.*) Were precipitated twice with molybdic solution to get rid of iron. The "white" precipitates giving results *c.* were free from iron, but *b* still contained some, as shown by color and chemical test.

A word may not be out of place here in regard to the titration and end reaction. The greater the amount of yellow precipitate present, the more slowly does the phenolphthalein color disappear, but up to 20 per cent., or more, when 0.2 gram of substance is used, the end reaction is quite sharp. For percentages much above twenty, I consider 0.1 gram substance better to use, when the end reaction will be found sharp for any percentages one will be called upon to work. To summarize: For percentages below five, use 0.4 gram substance (or about); for percentages between five and twenty, use 0.2 gram; and above twenty, use 0.1 gram.

It will also be found that by adding the indicator after the precipitate has been dissolved in the alkali that the molybdenum colorations which sometimes occur to interfere with the end reaction, will be avoided. This observation was made by Street in his work previously referred to, and my observations corroborate it. Of the results presented in the table, the gravimetric determinations were made by Messrs. W. M. Allen, H. K. Miller and myself, and the volumetric ones by myself.

The volumetric method was somewhat modified at the last meeting of the Association of Official Agricultural Chemists, and in such a way as to prevent the difficulty of excessive washing, mentioned in this paper. I repeat here the method in the form in which it was recommended by the Association for testing in the work of this year:

Dissolve 2 grams substance in nitric and hydrochloric acids, incinerating beforehand to destroy organic matter, if necessary, and make up to volume of 200 c. c. For percentages below 5, use 40 c. c. of solution, for percentages between 5 and 20 use 20 c. c. (and for percentages above 20 use 10 c. c.); add 5 to 10 c. c. concentrated nitric acid, nearly neutralize with ammonia, heat in water bath at 60°-65° c., add 50 c. c. freshly filtered molybdic solution for each decigram P_2O_5 present, and digest in water bath for 10 to 15 minutes.

Decant the clear liquid on the filter as quickly as possible, using Hirsch funnel with suction, or ordinary funnel and filter paper with or without pressure. Wash the precipitate by decantation twice with 10 per cent nitric acid solution, using about 50 c. c. of the solution each time, agitating thoroughly and allowing the precipitate to completely settle, once with the same amount of 3 per cent ammonium or potassium nitrate solution¹, and transfer it to the filter and wash it five or six times with water, using 150 to 250 c. c.² Now wash the filter and contents back into the beaker, add excess of standard alkali and then a few drops of phenolphthalein, and titrate back with standard nitric acid.

¹ It is suggested that water be used for this washing by decantation, instead of the nitrate solution.

² In our experience 200 c. c. of water is sufficient.